

In re Application of J.P. Haenen et al.

U.S. Appl. No. 10/530,084

Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

Listing of Claims:

1. (Original) A printing sheet comprising a substrate and, on at least one side of the substrate, an image receptive coating layer with a cumulative porosity volume of pore widths below 200nm as measured using nitrogen intrusion methods of more than 0.006 cm³ per gram paper.
2. (Currently Amended) Printing sheet according to claim 1, ~~characterised in that wherein~~ the cumulative porosity volume of pore widths below 200 nm is more than 0.008 cm³ per gram paper.
3. (Currently Amended) Printing sheet according to ~~one of the preceding claim 2s~~, ~~characterised in that wherein~~ the surface of the image receptive layer is substantially non-polar.
4. (Currently Amended) Printing sheet according to claim 3, ~~characterised in that wherein~~ the polar part of the surface energy of the surface of the image receptive layer is less than 7 mN/m, ~~preferably less than 6 mN/m~~ as determined by contact angle measurements at a Parker Print Surf (PPS) surface roughness of between 0.8 and 1.0 μ m, ~~preferably of less than 0.9 μ m~~, wherein preferentially the ~~polar part of the surface energy of the surface of the image receptive layer is more than 4 mN/m~~.
5. (Currently amended) Printing sheet according to ~~one of the preceding claim 1s~~, characterised by a gloss on the surface of the image receptive coating of more than 75 % according to TAPPI 75deg.

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

6. (Currently Amended) Printing sheet according to ~~one of the preceding claims~~ claim 1, characterised by a gloss on the surface of the image receptive coating of ~~more than 45, preferably more than 50%~~ according to DIN 75deg.
7. (Currently Amended) Printing sheet according to ~~one of the preceding claims~~ claim 1, ~~characterised in that~~ wherein an image receptive coating layer is provided on the both sides of the substrate.
8. (Currently Amended) Printing sheet according to ~~one of the preceding claims~~ claim 1, ~~characterised in that~~ wherein it has a specific volume of more than 0.8 cm³/g, ~~preferably of more than 0.82 or 0.85 cm³/g~~.
9. (Currently Amended) Printing sheet according to ~~one of the preceding claims~~ claim 1, characterised by an ink set-off of less than 0.3 at 30 secs, ~~preferably of~~ in the range of between 0.15 to 0.25 or of approx. 0.2 at 30 seconds.
10. (Currently Amended) Printing sheet according to ~~one of the preceding claims~~ claim 1, ~~characterised in that~~ wherein the image receptive coating layer comprises a top layer \leftrightarrow comprising:
 - a pigment part, wherein this pigment part is composed of
 - a) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than 100μm, ~~preferably with a particle size distribution such that approximately 90 % of the particles are smaller than 100μm,~~

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

b) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size distribution such that more than 90 % of the particles are smaller than 1 μ m, preferably with a particle size distribution such that more than 95 % of the particles are smaller than 1 μ m,

c) 0 to 20 parts ~~or up to 30 parts~~ in dry weight of a particulate, preferably solid or vacuolated polymer pigment with a particle size distribution such that more than 90 % of the particles are smaller than 0.5 μ m, preferably with a particle size distribution such that 90 % of the particles have sizes between 0.05 and 0.3 μ m, in particular between 0.1 and 0.2 μ m, or in the case of a vacuolated polymer pigment also with a mean particle size of about 0.6 μ m, wherein optionally the particulate polymer pigment may replace the inorganic pigments (a,c) completely or partially

and a binder part, wherein this binder part is composed of:

a') less than ~~12 to 16~~ parts in dry weight of binder and
b') less than 2 parts in dry weight of additives.

11. (Currently Amended) Printing sheet according to ~~one of the preceding claims~~ claim 11, ~~characterised in that~~ wherein the image receptive coating layer comprises a top layer (1) comprising:

a) pigment part, wherein this pigment part is composed of

a) 0 to 50 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than 1 μ m, ~~preferably with a particle size distribution such that approximately 90 % of the particles are smaller than 1 μ m,~~

b) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size distribution such that more than 90 % of the particles are smaller than 1 μ m,

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

~~preferably with a particle size distribution that more than 95 % of the particles are smaller than 1 •m,~~

c) 2 to 100 parts in dry weight of a particulate solid polymer pigment with a particle size distribution such that more than 90 % of the particles are smaller than 0.5 •m, ~~preferably with a particle size distribution such that 90 % of the particles have sizes between 0.05 and 0.3 •m, in particular between 0.1 and 0.2 •m,~~

and a binder part, wherein this binder part is composed of:

- a') less than ~~12 to 16~~ parts in dry weight of binder and
- b') less than 2 parts in dry weight of additives.

12. (Currently Amended) Printing sheet according to claim 10, ~~characterised in that~~ wherein ~~pigment part of the top layer (1)~~ comprises

a) 60 to 100 parts in dry weight, ~~preferably 65 to 80 parts in dry weight~~ of a fine particulate calcium carbonate with a particle size distribution such that approximately 90 % of the particles are smaller than 1 •m,

b) 10 to 40 parts in dry weight, ~~preferably 15 to 30 parts in dry weight~~ of a fine particulate kaolin with a particle size distribution such that 95 % of the particles are smaller than 1 •m,

c) 10 to 15 parts in dry weight of a solid particulate polymer pigment with a particle size distribution centred at approximately 0.13 to 0.17 •m, ~~preferably centred at approximately 0.14 •m, wherein 95 % of the particles are located within +/- 0.03 •m of this mean particle size.~~

13. (Currently Amended) Printing sheet according to ~~one of the claims 10 or 12,~~

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

~~characterised in that~~ wherein the solid particulate polymer pigment (c) is selected from the group consisting of: ~~poly(methyl methacrylate)~~, ~~poly(2-chloroethyl methacrylate)~~, ~~poly(isopropyl methacrylate)~~, ~~poly(phenyl methacrylate)~~, ~~polyacrylonitrile~~, ~~polymethacrylonitrile~~, ~~polycarbonates~~, ~~polyetheretherketones~~, ~~polyimides~~, ~~acetals~~, ~~polyphenylene sulfides~~, ~~phenolic resins~~, ~~melamine resins~~, ~~urea resins~~, ~~epoxy resins~~, ~~polystyrene latexes~~, ~~polyacrylamides~~, and ~~alloys, blends, mixtures and derivatives thereof~~.

14. (Currently Amended) Printing sheet according to ~~one of the claim 12s 10 to 13~~, ~~characterised wherein the solid particulate polymer pigment (c) is poly(methyl methacrylate)~~ in that the solid particulate polymer pigment (c) is a modified ~~polystyrene latex~~.
15. (Currently Amended) Printing sheet according to ~~one of the claim 12s 10 to 14~~, ~~characterised in that~~ wherein the solid particulate polymer pigment (c) is based on styrene maleic acid copolymeric latexes (SMA) and/or styrene malimide copolymeric latexes (SMI) ~~preferably based almost exclusively on styrene malimide copolymeric latexes (SMI) with glass transition temperatures in the range of 200° C.~~
16. (Currently Amended) Printing sheet according to ~~one of the claim 12s 10 to 15~~, ~~characterised in that~~ wherein the binder part of the top layer (1) comprises
 - a') a binder selected from the group consisting of latex, in particular styrene-butadiene, styrene-butadiene-acrylonitrile, styrene-acrylic, styrene-butadiene-acrylic latexes, starch, polyacrylate salt, polyvinyl alcohol, soy, casein, carboxymethyl cellulose, hydroxymethyl cellulose and mixtures thereof,
 - b') additives like defoamers, colorants, brighteners, dispersants, thickeners,

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

water retention agents, preservatives, crosslinkers, lubricants and pH control agents.

17. (Currently Amended) Printing sheet according to claim 16, ~~characterised in that~~ ~~wherein~~ the binder is an acrylic ester copolymer based on butylacrylate, styrene and acrylonitrile.
18. (Currently Amended) Printing sheet according to ~~one of the claim 16s 16 to 17~~ ~~characterised in that~~ ~~wherein~~ 10 to 16 parts in dry weight, preferably 11 to 14 parts in dry weight of binder (a') is present in the binder part.
19. (Currently Amended) Printing sheet according to ~~one of the claim 10s 10 to 18~~, ~~characterised in that~~ ~~wherein~~ the top layer (1) has a total dried coat weight of in the range of 3 to 25 g/m², preferably in the range of 4 to 15 g/m², and most preferably of about 6 to 12 g/m².
20. (Currently Amended) Printing sheet according to ~~one of the claim 10s 10 to 19~~, ~~characterised in that~~ ~~wherein~~ the image receptive coating layer has a second layer (2) beneath said top layer (1) comprising:
 - (i) pigment part, wherein this pigment part is composed of
 - A) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle size distribution such that more than 80 % of the particles are smaller than 100μm, preferably with a particle size distribution such that approximately 90 % of the particles are smaller than 100μm,
 - B) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

distribution such that more than 50 % of the particles are smaller than 1 μm , ~~preferably with a particle size distribution that more than 60 % of the particles are smaller than 1 μm , or alternatively of a fine particulate carbonate with a particle size distribution such that more than 70% of the particles are smaller than 1 μm ,~~

and a binder part, wherein this binder is composed of:

A') less than 20 parts in dry weight of binder and

B') less than 4 parts in dry weight of additives.

21. (Currently Amended) Printing sheet according to claim 20, ~~characterised in that~~ ~~wherein~~ the pigment part of the second layer (2) comprises

A) 70 to 90 parts in dry weight, ~~preferably approx. 75 parts in dry weight~~ of a fine particulate calcium carbonate with a particle size distribution such that approximately 90 % of the particles are smaller than 1 μm ,

B) 20 to 40 parts in dry weight, ~~preferably approx. 25 parts in dry weight~~ of a fine particulate kaolin with a particle size distribution such that 65 % of the particles are smaller than 1 μm or alternatively 50 to 70 parts of a fine particulate carbonate with a particle size distribution such that more than 70% of the particles are smaller than 1 μm .

22. (Currently Amended) Printing sheet according to ~~one of the~~ claim 20s to 21, ~~characterised in that~~ ~~wherein~~ the binder part of the second layer (2) comprises

A') a binder selected from the group consisting of latex, in particular styrene-butadiene, styrene-butadiene-acrylonitrile, styrene-acrylic, styrene-butadiene-acrylic latexes, starch, polyacrylate salt, polyvinyl alcohol, soy, casein,

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

carboxymethyl cellulose, hydroxymethyl cellulose and mixtures thereof,

B') additives like defoamers, colorants, brighteners, dispersants, thickeners, water retention agents, preservatives, crosslinkers, lubricants and pH control agents.

23. (Currently Amended) Printing sheet according to claim 22, ~~characterised in that wherein~~ the binder is an acrylic ester copolymer based on butylacrylate and styrene.

24. (Currently Amended) Printing sheet according to ~~one of the claim 20s to 23,~~ ~~characterised in that wherein~~ 6 to 20 parts in dry weight, ~~preferably 8 to 14 parts in dry weight, and most preferably approximately 10 parts in dry weight~~ of binder is present in the binder part (A') of the second layer (2).

25. (Currently Amended) Printing sheet according to ~~one of the claim 20s to 24,~~ ~~characterised in that wherein~~ the second layer (2) has a total dried coat weight of in the range of 5 to 25 g/m², ~~preferably in the range of 8 to 20 g/m²~~.

26. (Currently Amended) Printing sheet according to ~~one of the claim 20s to 25,~~ ~~characterised in that wherein~~ beneath the second layer (2) there is a third layer (3) which is composed of:
i) pigment part, wherein this pigment part is composed of
AA) 50 to 100 parts in dry weight of a particulate carbonate with a particle size distribution such that more than 70 % of the particles are smaller than 100μm, ~~preferably with a particle size distribution such that approximately or~~

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: CO/ TED PRINTING SHEET
AND PROCESS FOR MAKING SAME

~~more than 80 % of the particles are smaller than 1•m,~~
and a binder part, wherein this binder is composed of:
AA') less than 10 parts in dry weight of binder and
BB') less than 4 to 6 parts in dry weight of additives.

27. (Currently Amended) Printing sheet according to ~~one of the preceding claim 20_s,~~
~~characterised in that~~wherein its total weight is in the range of 90 or 100 to ~~250 g/m²~~
~~or up to 400 g/m².~~

28. (Currently Amended) Printing sheet according to ~~one of the preceding claims~~claim
1 ~~characterised in that~~wherein the substrate (5) is provided with an image receptive
coating on both sides.

29. (Currently Amended) A method of manufacturing a printing sheet comprising:
d) applying an image receptive top of layer (1) on the substrate said top layer (1)
comprising:
a pigment part, wherein this pigment part is composed of
a) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle
size distribution such that more than 80 % of the particles are smaller than
~~1•m, preferably with a particle size distribution such that approximately 90~~
~~% of the particles are smaller than 1•m,~~
b) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size
distribution such that more than 90 % of the particles are smaller than 1 •m;

In re Application of J.P. Haenen et al.
U.S. Appln. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

~~preferably with a particle size distribution that more than 95 % of the particles are smaller than 1 μ m,~~

c) 0 to 20 parts ~~or up to 30 parts~~ in dry weight of a particulate, preferably solid or vacuolated polymer pigment with a particle size distribution such that more than 90 % of the particles are smaller than 0.5 μ m, ~~preferably with a particle size distribution such that 90 % of the particles have sizes between 0.05 and 0.3 μ m, in particular between 0.1 and 0.2 μ m, or in the case of a vacuolated polymer pigment also with a mean particle size of about 0.6 μ m,~~ wherein optionally the particulate polymer pigment may replace the inorganic pigments (a,c) completely or partially,

and a binder part, wherein this binder part is composed of:

a') less than 10 parts in dry weight of binder and

b') less than 2 parts in dry weight of additives

(e) drying the image receptive coating layer

(f) calendering at a nip pressure of less than 200 N/mm at a temperature of less than 180 degrees Celsius.

30. (Currently Amended) A method according to claim 29, wherein the top layer (1) has a total dried coat weight of in the range of 3 to 25 g/m², ~~preferably in the range of 4 to 15 g/m², and most preferably of about 6 to 12 g/m².~~

31. (Currently Amended) A method according to ~~one of the~~ claim 29 or 20, characterised in an image receptive coating and in particular comprising a top layer according to ~~one of the~~ claim 15 to 17.

In re Application of J.P. Haenen et al.
U.S. Appln. No. 10/530,084
Title: COATED PRINTING SHEET
AND PRC CESS FOR MAKING SAME

32. (Currently Amended) A method according to ~~one of the claims 29 to 31~~ claim 31,
~~characterised in that~~ wherein prior to the application of the top coat layer (1)

c) a second layer (2) is applied on the substrate, said second layer (2) beneath said
top layer (1) comprising preferentially:

a pigment part, wherein this pigment part is composed of

A) 50 to 100 parts in dry weight of a fine particulate carbonate with a particle
size distribution such that more than 80 % of the particles are smaller than
~~1.00m, preferably with a particle size distribution such that approximately 90~~
~~% of the particles are smaller than 1.00m,~~

B) 0 to 50 parts in dry weight of a fine particulate kaolin with a particle size
distribution such that more than 60 % of the particles are smaller than 1.00m,
~~preferably with a particle size distribution that more than 70 % of the~~
~~particles are smaller than 1.00m, or alternatively of a fine particulate~~
carbonate with a particle size distribution such that more than 70% of the
particles are smaller than 1.00m,

and a binder part, wherein this binder is composed of:

A') less than 20 parts in dry weight of binder and

B') less than 4 parts in dry weight of additives

33. (Currently Amended) A method according to claim 32, wherein the second layer (2)
has a total dried coat weight of in the range of 5 to 25 g/m², ~~preferably in the range~~
~~of 8 to 20 g/m².~~

34. (Currently Amended) A method according to claim 32 ~~one of the claims 32 or 33~~,
~~characterised in a second layer (2) according to claim 20 ~~one of the claims 19 to 24~~.~~

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

35. (Currently Amended) A method according to claim 29 ~~one of the claims 22 to 34, characterised in that~~ wherein prior to the application of the second layer (2) b) a third layer (3) is applied on the substrate, said third layer (3) beneath said second layer (2) comprising:

AA) 50 to 100 parts in dry weight of a particulate carbonate with a particle size distribution such that more than 70 % of the particles are smaller than 1••m, ~~preferably with a particle size distribution such that approximately or more than 80 % of the particles are smaller than 1••m,~~

and a binder part, wherein this binder is composed of:

AA') less than 10 parts in dry weight of binder and

BB') less than 4 to 6 parts in dry weight of additives.

36. (Currently Amended) A method according to claim 35, ~~characterised in that~~ wherein prior to the application of the third layer (3) a sizing layer (4) is applied to the substrate (5).

37. (Currently Amended) A method according to claim 29 ~~one of the claims 29 to 36, characterised in that~~ wherein the image receptive coating is applied on both surfaces of the substrate (5).

38. (Currently Amended) A method according to claim 29 ~~one of the claims 29 to 37, characterised in that~~ wherein the resulting printing sheet has a total weight in the range of 80 to 400 g/m², ~~preferentially of 100 to 250 g/m²~~ after the coating process.

In re Application of J.P. Haenen et al.
U.S. Appl. No. 10/530,084
Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

39. (Currently Amended) A method according to claim 29 to one of the claims 29 to 38, ~~characterised in that wherein~~ in the calendering step (ff) a nip pressure of in the range of 60 to 150 N/mm, ~~preferentially of 90 to approximately 110 N/mm~~ is being used.

40. (Currently Amended) A method according to claim 29 one of the claims 29 to 39, ~~characterised in that wherein~~ in the calendering step (ff) a temperature of in the range of 45 to 80 degree Celsius, ~~preferably in the range of 50 to 70 degree Celsius~~ is being used.

41. (Currently Amended) A method according to claim 29 one of the claims 29 to 40, ~~characterised in that wherein~~ 4 nips or less are being used in the calendering step (ff).

42. (Currently Amended) A method according to claim 29 one of the claims 29 to 41, ~~characterised in that wherein~~ in the calendering step (ff) rolls of steel or fibre surface are being used at a speed of 300 to 1000 m/min.

43. (Currently Amended) A method according to claim 29 one of the claims 29 to 41, ~~characterised in that wherein~~ prior to the calendering (ff) of the printing sheet is dried to a moisture of less than 5%.

44. (Currently Amended) Use of a printing sheet according to ~~one of the claims 1 to 28~~ in an offset printing process.

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In re Application of J.P. Haenen et al.

U.S. Appl. No. 10/530,084

Title: COATED PRINTING SHEET
AND PROCESS FOR MAKING SAME

89. (New) Printing sheet according to claim 16, wherein the solid particulate polymer pigment (c) is based almost exclusively on styrene malimide copolymeric latexes (SMI) with glass transition temperatures in the range of 200 °C.

90. (New) Printing sheet according to Claim 4, wherein the polar part of the surface energy of the surface of the image receptive layer is more than 4mN/m.